THE EFFECT OF DIFFERENT COUPLING AGENT ON ZEOLITE MODIFICATION FOR DEVELOPMENT OF POLYETEHERSULFONE MMMs FOR O_2/N_2 SEPARATION.

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ABSTRACT

The industrial gas separations have been attracted in using membrane for gas separations since membrane separation technologies have the advantages of energy efficiency, simplicity and low cost. This lead to the exploration mixed matrix membrane (MMMs) that combining the polymeric membrane filled with organics particles. In order to improve the interaction between polymer and zeolite, chemical modification on the surface of zeolite using silane coupling agents need to be done to increase the compatibility between zeolite and polymer. In this study, the effect of difference coupling agents used on zeolite modification in development of Polyethersulfone MMMs for O_2/N_2 separation was studied. Three types of coupling agents were used which are 3-aminopropyltriethoxysilane, glycidoxypropyltrimethoxysilane and 3-aminopropyltrimethoxy- silane (APTMOS). The polymer solution was prepared contains of 30% Polyethersulfone (PES) as the polymer, 55% of N-Methyl Pyrolidone (NMP) as the solvent and 15% of zeolite 5A. The dry/wet phase inversion method was used to produce the membrane. The membrane was coated with silicone and n-hexane in order to decrease the surface defect and tested using O_2 and N_2 gases to determine the membrane performance. For surface and cross section image of membrane were identified using Scanning Electron Microscope (SEM). Membrane was also characterized using Fourier Transform Infrared Spectroscopy (FTIR) to analyze the presence of silane coupling agent functional group. As a conclusion, the best performance was identified by using glycidoxypropyltrimethoxysilane which gives high selectivity about 3.14.

ABSTRAK

Industri pemisahan gas telah menarik minat menggunakan membran bagi memisahkan gas. Antara kelebihan menggunakan teknologi membran adalah penggunaan tenaga secara efisyen, mudah dan kos yang rendah. Ini membawa kepada penerokaan campuran membran matrik yang menggabungkan membran polimer dengan zeolit. Bagi meningkatkan keserasian antara polimer dan zeolit, pengubahsuaian permukaan zeolit menggunakan ejen gabungan silan perlu dilakukan. Dalam kajian ini, kesan penggunaan ejen gabungan silan yang berlainan dalam pengubahsuaian permukaan zeolit untuk menghasilkan campuran membran matrik Poliethersulfona (PES) bagi memisahkan oksigen dan nitrogen telah dikaji. Tiga jenis ejen gabungan silana telah digunakan iaitu 3-aminopropyltriethosisilan, glycidosipropyltrimethosisilan and 3-aminopropyltrimethosisilan. Campuran polimer yang mengandungi 30% Poliethersulfona (PES) sebagai polimer, 55% N-MetilPyrolidona (NMP) sebagai bahan pelarut dan 15% zeolit 5A telah disediakan. Untuk menghasilkan membran ini proses fasa balikan kering/basah telah digunakan. Membran yang terhasil akan disalut dengan silikon dan N-Heksana untuk tujuan mengurangkan kecacatan pada permukaan membran. Membran yang terhasil diuji dengan menggunakan gas oksigen dan nitrogen. Permukaan dan imej keratan rentas membran telah dikaji menggunakan Mikroskop Pengimbas Elektron (SEM). Membran telah dianalisa menggunakan Spektroskopi Infra-Merah Fourier (FTIR) untuk mengkaji kehadiran kumpulan ejen gabungan silana. Dapat diputuskan bahawa penggunaan glycidosipropyltrimethosisilan memberi kadar pemilihan yang paling tinggi iaitu sebanyak 3.14.

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LIST OF SYMBOLS

P	Overall permeability
Pc	Permeability of the continuous polymer phase
Pd	Permeability of the dispersed zeolite phase
Ø	Volume fraction
α	Selectivity (Unitless)
Q	Flow rate of gas species
A	Area of membrane
ΔP	Pressure difference across membrane (cm Hg)
Å	Amstrong
nm	Nanometer
µm	Micrometer
cm	Centimeter
mL	Milliliter
%	Percentage
Kg	Kilogram
g	Gram
°C	Degree celcius
K	Kelvin
F	Fahrenheit
kPa	Kilopascal
(P/*l*)	Pressure Normalized Flux (cm^3 (STP)/ cm^2. s. cmHg)

LIST OF ABBREVIATIONS

CMS	Carbon molecular sieves
O_2	Oxygen
N_2	Nitrogen
wt%	Weight percentage
PES	Polyethersulfone
MMMs	Mixed Matrix Membranes
APTES	3-aminopropyltriethoxysilane
GPTMS	Glycidoxypropyltrimethoxysilane
APTMOS	3-aminopropyltrimethoxysilane
SEM	Scanning Electron Microscopic
STP	Standard Pressure and Temperature
GPU	Gas Permeation Unit
AlO_4	Aluminium Oxide
SiO_4	Silicone Oxide
NMP	N-methyl-2-Pyrolidone
H_2O	Water
PDMS	Polydimethylsiloxane
FTIR	Fourier Transform Infrared Spectroscop

CHAPTER 1

INTRODUCTION

1.1 Research Background

During the past 20 years, gas separation has become main industrial application of membrane technology (Baker, 2004). Gas separation is an important unit operation and widely use in chemical industries. For examples the separation of air into oxygen and nitrogen and the removal of volatile organic compounds from effluent streams. The traditional method that use for gas separation include cryogenic distillation and adsorbent bed process. Recently, membrane based gas separation has been used (Javaid, 2005).

Membrane based gas separation widely used due to its inherent advantages compare to traditional method, low capital and operating costs, lower energy requirements and ease of operation (Chung *et al*., 2007). Membrane based process has been used in wide array of application such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. There are some limitations for polymer membrane which are poor contaminant resistance, low chemical and thermal stability. In addition polymer membrane materials reached a limit in the tradeoff between productivity and selectivity (Kulprathipanja, 2010).

Then research is focused on forming novel membranes such as nanoporous molecular sieving material. Example of nanoporous molecular sieving such as carbon molecular sieves (CMS), silica and zeolite. The selectivity and permeability for carbon membrane is higher than polymer membrane. In spite of these findings carbon membrane not widely used in industrial separation process due to the inherent brittleness of carbon material, high price and aging of the carbon surface by chemical surface reaction (Nunes and Peinemann, 2006).

Then mixed matrix membrane has been proposed as an alternative approach to obtain high selectivity and permeability from molecular sieving membranes and economical processing of polymer (Vu *et al*., 2003). The fragility inherent in organics membrane can be avoided by using flexible polymer as continuous matrix. Mixed matrix membrane is an organic –inorganic membrane consists of dispersed inorganics particles such as zeolite particles in continuous organic polymer. Mixed matrix membrane provide the advantages of both inorganic and organics membrane (Kulprathipanja, 2010).

Zeolites also known as molecular sieves are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium and calcium. The development of a successful mixed matrix membrane depends on good match and compatibility between zeolite and polymer material. There are some obstacles in producing successful mixed matrix membrane which is poor adhesion between polymer and zeolite particles which produce voids and defects in membrane. To overcome this problem, coupling agents has been used to improve adhesion between zeolite and polymer (Kulprathipanja, 2010).

For zeolite surface modification, usually use silane coupling agents such as 3-aminopropyltriethoxysilane, 3-aminopropyl-trimethoxysilane, *N*-β-(aminoethyl)-γ-aminopropyltrimethoxy silane, (γ - glycidyloxypropyl)-trimethoxy silane and (3-aminopropyl)-dimethylethoxy silane. 3-aminopropyltriethoxysilane consists of three ethoxy group and for 3-aminopropyl-trimethoxysilane it consists of three methoxy group. Both of the coupling agents consist of amino functional group and for (γ - glycidyloxypropyl)-trimethoxy silane it consists of epoxy functional group. Ethoxy and

methoxy group is a hydrozable group. Silanol group was produce through hydrolysis reaction. The silanol groups will react with hydroxyl group found on zeolite surface to form siloxane bonds through condensation reaction.

From a research on enhanced gas permeation performance of polyethersulfone mixed matrix hollow fibre membranes using novel Dynasylan Ameo silane agent show that with membrane with modified zeolite, gas separation performance higher compare to membrane with unmodified zeolite. Selectivity of O_2/N_2 for untreated zeolite was lowest compare to treated zeolite which is 2.13. For 10wt% of treated zeolite the selectivity was 2.74, 15 wt % of treated zeolite the selectivity was 3.07 and 20 wt% of treated zeolite the selectivity was 4.78. Therefore, by using coupling agents, it will expect to increase the selectivity of gas separation. By using different coupling agents give different selectivity of gas. For hollow fiber 3-aminopropyltriethoxysilane selectivity of O_2/N_2 was 4.78 (Ismail *et al*., 2008). For 3-aminopropyltrimethoxsilane the selectivity of O_2/N_2 was 3.25 (Hidayat, 2010).

1.2 Problem statement

Membrane separation process have widely use especially for gas and liquid separations. Gas and liquids separation process required a membrane with high permeability and selectivity. Currently, carbon molecular sieve and zeolite had been embedded in polymer matrix due to their excellent separation performances for the gases. In mixed matrix membranes fabrication, the most important thing is to ensure there is a good contact between polymer matrix and zeolite.

For PES, it is widely used for gas separations due to the wide operating temperature, limit, wide operating pH tolerances, fairly good chlorine resistance, easy fabrication in wide variety of configuration and good chemical resistance to aliphatic hydrocarbons, alcohol and acids. But in PES, there is disadvantage which is poor compatibility between zeolite and polymer matrix. In this research, we need to study the effect of different coupling agents on zeolite modification for PES MMMs in order to obtain a good performance of membrane.

1.3 Objectives

Based on the problem statement, the objectives of this study are:

a) To develop Polyethersulfone Mixed Matrix Membranes for O_2/N_2 separation.
b) To study the effect of difference coupling agents used on zeolite modification in development of Polyethersulfone Mixed Matrix Membranes for O_2/N_2 separation.

1.4 Scope of study

There are several scopes of study that have been outlined to achieve the objectives of this study which are:

a) Three types of coupling agents were used which are 3-aminopropyltriethoxysilane (APTES), glycidoxypropyltrimethoxysilane (GPTMS) and 3-aminopropyltrimethoxy- silane (APTMOS).
b) Preparing asymmetric mixed matrix membrane by phase inversion technique using dope solution contain of Polyethersulfone (polymer) and N-methyl-2-Pyrolidone (solvent).
c) Characterize the membranes morphology using Scanning Electron Microscopy (SEM).
d) Characterize the functional group in membranes using Fourier Transform Infrared Spectroscopy (FTIR)

1.5 Rational and significance

To improve the interfacial strength to enhance the separation performance is to use chemical modification of zeolite surface with coupling agent. Different coupling agents have different effect on the voids between zeolite and polymer. The presence of void at polymer- zeolite interface reducing the separation performance of the membrane. By using coupling agents, the selectivity of gas will increase and can achieve better gas separation. By achieve better gas separation, can save cost and energy.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background of membranes

Nowadays membrane gained an important place in chemical technology and used widely like in hydrogen separation, oxygen-nitrogen separation, natural gas separation, vapor-vapor separation and dehydration of air (Baker, 2006). The development of membrane dates back to early 18^{th} century and has been developing rapidly. In 1784, Abbé Nolet started to use the word osmosis to describe permeation of water through a diaphragm. At nineteenth and early twentieth century, membrane uses limited at laboratory tools in developing physical and chemistry theories only (Baker 2006). Table 2.1 shows the events of the development of membrane technology.

Table 2.1: Events of the development of membrane technology.

Year/ century	Researcher	Inventor
1748	Abbé Nolet	Introduced the word osmosis to describe water permeation through water
1829	Thomas Graham	Performed first recorded experiment on the transport of gases and vapors in polymeric membranes
1855	Fick	Proposed quantitative description of material transport through boundary layer
1887	Van‟t Hoff	Explain the behavior of ideal dilute solutions and introduce Van‟t Hoff equation
	Maxwell et al	Develop Kinetic theory of gases
1907	Bechold	Devised a technique in preparation nitrocellulose membrane of graded pore size using a buble test
1930	Ekford, Zsigmondy, Bachmann and Ferry	Improved Bechhhold's technique and microporous colloidion membrane commercially available
1960	Loeb–Sourirajan	Develop process for making defect free, high flux, anisotropic reverse osmosis membranes.
1966	Alex Zaffaroni	Use membranes technique to control drug delivery system
1980		-Microfiltration, ultrafiltration, reverse osmosis and electrodialysis widely established -Monsanto Prism develops membrane for hydrogen separation.
1980	GFT (German engineering company)	Introduce commercial pervaporation systems for dehydration of alcohol

Source: Baker (2006)

2.2 Membrane Separation Technology

Membrane can be defined as a barrier which separates two phases and transport of various chemicals in a selective manner (Ravanchi *et al*., 2009). Membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure. Homogeneous is completely uniform in composition and structure and heterogeneous consists of holes or pores of finite dimensions or consisting if layered structured (Baker, 2006). Transport through the membrane take place when there is driving force applied to the components in the feed. In membrane processes, driving force can be defined as a pressure difference or a concentration difference across the membrane. Another driving force is electrical potential difference (Ravanchi *et al*., 2009).

The separation of gas mixture with membrane is rapidly growing and become one of significant unit operations in the chemical industry (Nunes and Peinemann , 2006). In membrane based gas separation, components separated from mixture by differential permeation through membranes. There are some advantages of membrane based technology such as low capital cost and high energy efficiency compare to older technique like crygogenic distillation, absorption and adsorption (Chung *et al*., 2007).

The membrane performance for separations is characterized by permeability across the membrane and selectivity. Selectivity can be defined as the ratio of permeabilities of feed component across the membrane. Permeability and selectivity are temperature dependent. For membrane mechanism, each feed component is sorbed by the membrane at interface, transported by diffusion across membrane through the voids between polymer chains and desorbed at other interface.

Membrane can be classified into two groups according to its morphology which are symmetric and asymmetric. Symmetric membrane is film without pores. Symmetric membrane significantly low permeability and hardly to practical uses. Asymmetric membrane structure consists of dense skin layer and a porous support layer (Li *et al*., 2008). Asymmetric membrane structure is shown in Figure 2.1. To maximize the membrane productivity needs to minimize the thickness of the membrane selective skin layer. Polymer membranes for gas separation have the geometry of an asymmetric flat sheet, a thin film composite or an asymmetric hollow fibre. These membranes have highly porous non- selective support layer and an ultrathin selective layer less than 100nm. Ultrathin selective layer provide membrane selectivity while highly porous non selective provide membrane mechanical strength. The membrane with thinner selective layer will have higher productivity compare to thicker layer (Kulprathipanja, 2010).

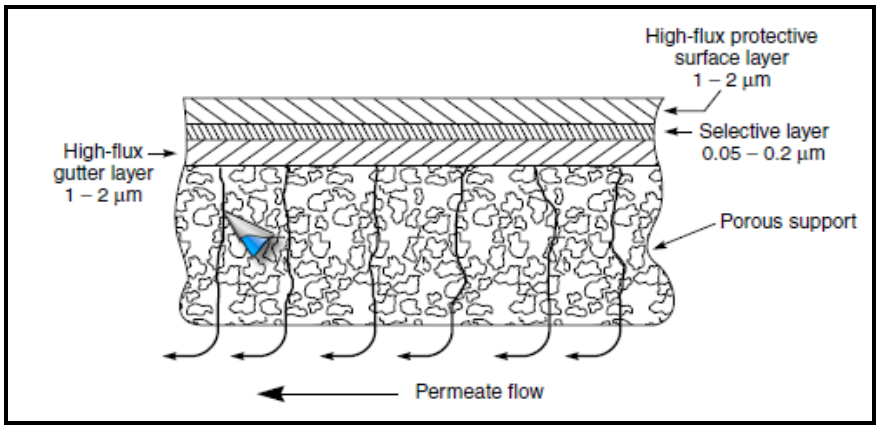

Figure 2.1: Asymmetric membrane structure

Sorce: Kulprathipanja (2010)

2.3 Mechanism for gas separation

There were various mechanisms for gas transports across membranes have been proposed depending on the properties of permeant and the membrane. The mechanism for gas separation is divided into porous membranes and dense membranes. The

mechanisms include Knudsen diffusion, the molecular sieve effects and a solution diffusion mechanism. However, most of these models have been found to be applicable only to a limited number of gas/material systems (Pandey and Chauhan, 2001). As a practical material, solution diffusion based gas transport through membrane is used exclusively in current commercial devices (Shu Shu, 2007). Figure 2.2 shows mechanism for permeation of gases through membranes.

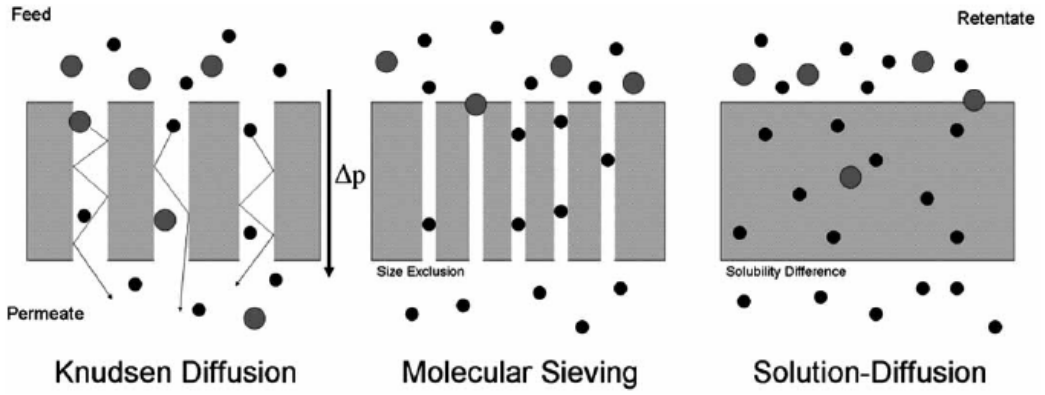

Figure 2.2: Mechanism for permeation of gases through membranes.

Source: Shu Shu (2007)

In molecular diffusion, the mean free path of the gas molecules is smaller than the pore size. Diffusion occurs primarily through molecule-molecule collisions. In this mechanism, the driving force is the composition gradient. If a pressure gradient is applied in such pore regimes bulk (laminar) flow occurs, as given by Poiseuille flow or viscous flow. For Knudson diffusion, the separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight (Javaid, 2005).

Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules (Colin *et al*., 2008). The diffusion mechanism is illustrated in

Figure 2.3. Zeolites are able to discriminate even in size and shape which gives superb gas separation efficiency. When one gas molecule is able to transverse the pore structure while the other is precluded due to oversize, the selectivity could ideally reach infinity (Shu Shu, 2007).

Figure 2.3: Illustration of gas molecule diffusion through a molecular sieve material

Source: Shu Shu (2007)

In dense membrane, solution diffusion widely accepted as mechanism of transport. This mechanism consist three steps of process. For first step the gas molecules are absorbed by the membrane surface on the upstream end. Second step was followed by the diffusion of the gas molecules through the polymer matrix. Finally the gas molecules evaporate on the downstream end (Javaid, 2005)

2.3 Mixed matrix membrane

During the last 2 decades, polymer based organic and inorganic get worldwide attention due to the superior performance in term of mechanical toughness permeability and selectivity for gas separation and photoconductivity for electronics. This concept has been use for gas liquid separation membrane by combine organic and inorganic material which called as mixed matrix membrane (Li *et al*., 2006). Mixed matrix membrane can be defined as the hybrid membrane which consists of inorganic molecular sieves (zeolite) and polymer. This membrane is a combination of selectivity of zeolite membranes with the low cost and ease of manufacture of polymer membranes. For performances of polymeric membranes in gas separation there is an

upper limit which predicted by Robeson in early 1990. Figure 2.4 shows the performance of various membrane materials available for the separation of O_2/N_2.

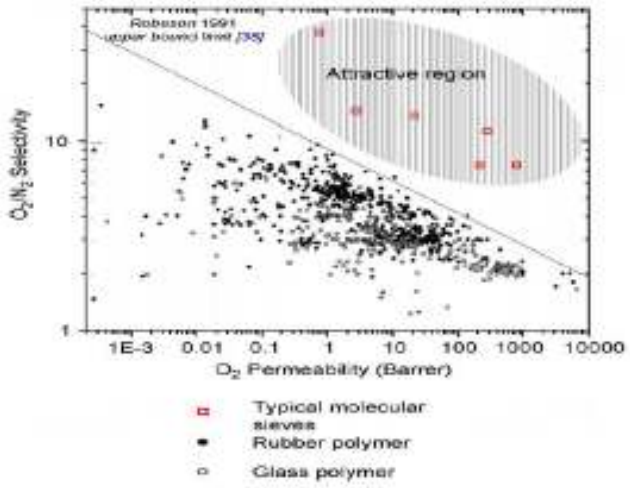

Figure 2.4: Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes

Source: Robeson (1991)

From Figure 2.4, it shows that for polymeric materials trade off exists between permeability and selectivity with an upper-bound limit. For polymeric membrane, the permeability and selectivity is tracking along this line instead of exceeding it. On the other hand, the inorganic materials properties lying far beyond the upper bound limit. The application of inorganic membrane is hindered by the lack of technology to form continuous and defect free membranes, the extremely high cost for membrane production and handling issue. A new approach is needed to provide cost effective membrane with separation properties well above the upper bound limit. The latest membrane with the potential for future applications is mixed matrix membrane (MMMs) which consists of organic polymer and inorganic particle (Chung *et al*., 2007).

In the development of mixed matrix membrane, proper selection for polymer as continuous phase and inorganics as dispersed phase properties is important which it can affect membrane morphology and separation performance. Mixed matrix membranes have higher selectivity compare to continuous polymer matrix. For MMMs fabrication

there were two inorganics phase material that have been use which are non porous and porous filler. For porous filler, zeolite and carbon molecular sieves (CMS) were commonly used. These materials have hydrophobic internal surface that used in industry to separate air by adsorption of oxygen and remove carbon dioxide. The additional of small volume fraction of zeolite to polymer matrix can increase the separation efficiency (Aroon *et al*., 2010). At low loadings of zeolite, permeation occurs by combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. The concept is show in Figure 2.5.

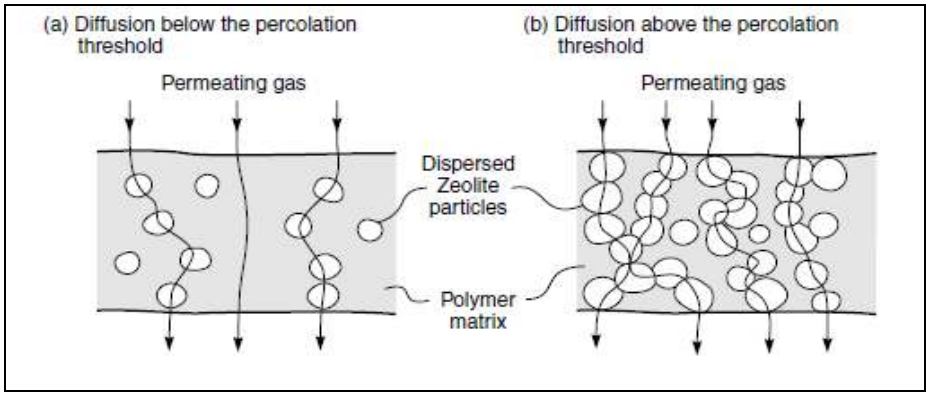

Figure 2.5: Gas permeation through mixed matrix membranes containing different amounts of dispersed zeolite particles

Source: Baker (2004)

At low loading of zeolite, the effect of permeable zeolite on permeation can be expressed mathematically by the expression shown below which develop by Maxwell in 1870s. For the equation 2.1, P is the overall permeability of mixed matrix membrane material, $\emptyset$ is the volume fraction of the dispersed zeolite phase, Pc is the permeability of the continuous polymer phase and Pd is the permeability of the dispersed zeolite phase.

$$P=Pc\,\frac{(Pd+2Pc-2\emptyset\,(Pc-Pd))}{(Pd+2Pc+\emptyset\,(Pc-Pd))} \qquad (2.1)$$